

(12) UK Patent Application (19) GB (11) 2 205 089 (13) A  
(43) Application published 30 Nov 1988

(21) Application No 8811393

(22) Date of filing 13 May 1988

(30) Priority data  
(31) 3717187 (32) 22 May 1987 (33) DE

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C01F 11/46

(52) Domestic classification (Edition J):  
C1A 421 423 424 D45 G47 G47D45 PF9B  
U1S 1399 1694 C1A

(56) Documents cited  
None

(58) Field of search  
C1A  
Selected US specifications from IPC sub-class  
C01F

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(54) Process for production of calcium sulphate alpha-hemihydrate

(57) A process for the production of calcium sulphate alpha-hemihydrate from finely divided calcium sulphate dihydrate by recrystallising the calcium sulphate dihydrate in the presence of saturated water vapour, in which process the calcium sulphate dihydrate is prepared in the form of mouldings containing 15 to 60 vols. % of pores and more than 5 vol. % air in the pores (all percentages relating to the volume of a single moulding). The mouldings are placed in an autoclave. In the presence of an adequate amount of water in the pores, the crystal growth and crystal form of the calcium sulphate alpha-hemihydrate, which grows in and form an aqueous solution phase, are controlled by maintaining a temperature between 110°C and 180°C and regulating the atmospheric pressure inside the autoclave. After recrystallisation, the mouldings are taken out of the autoclave and used as required.

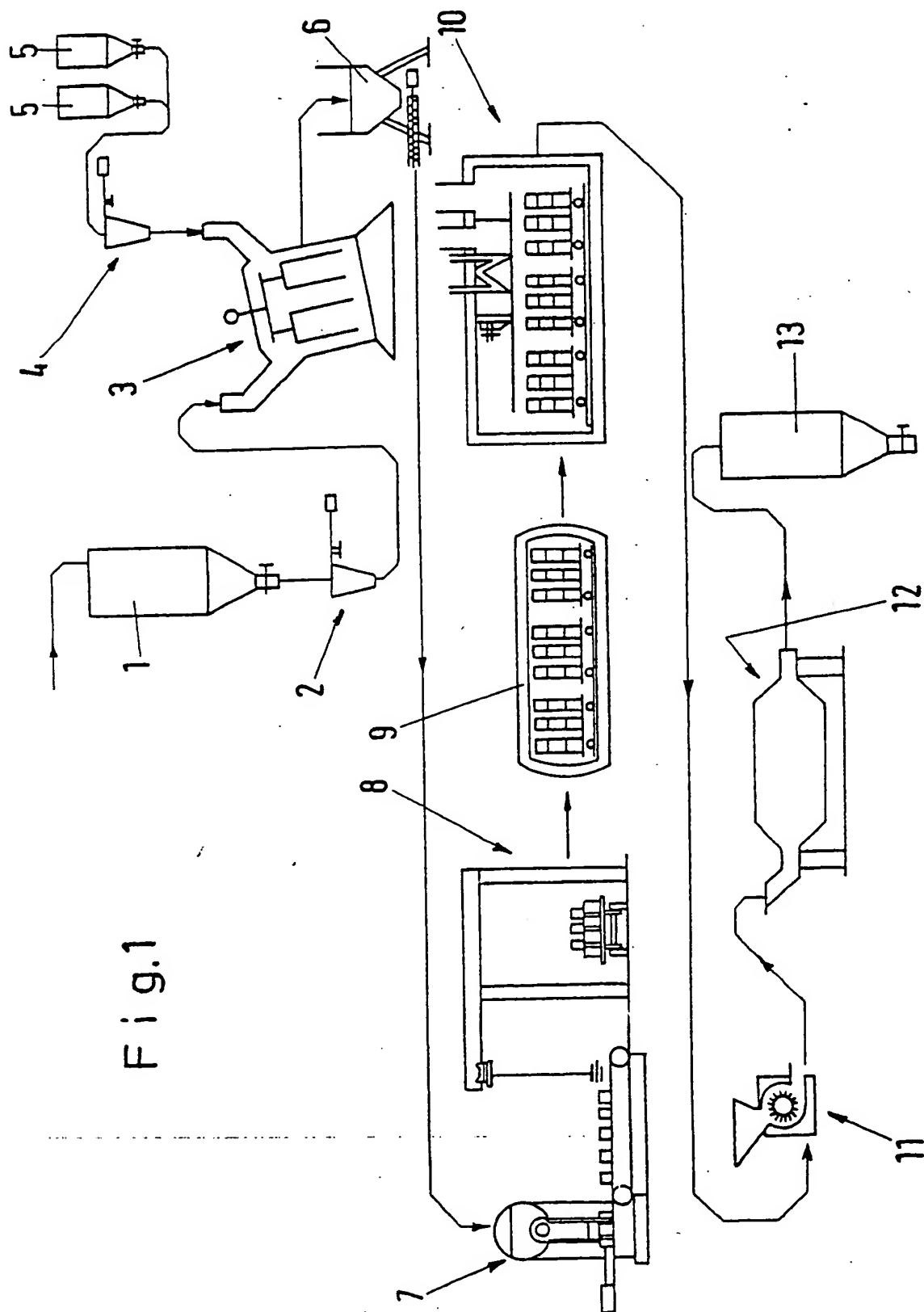
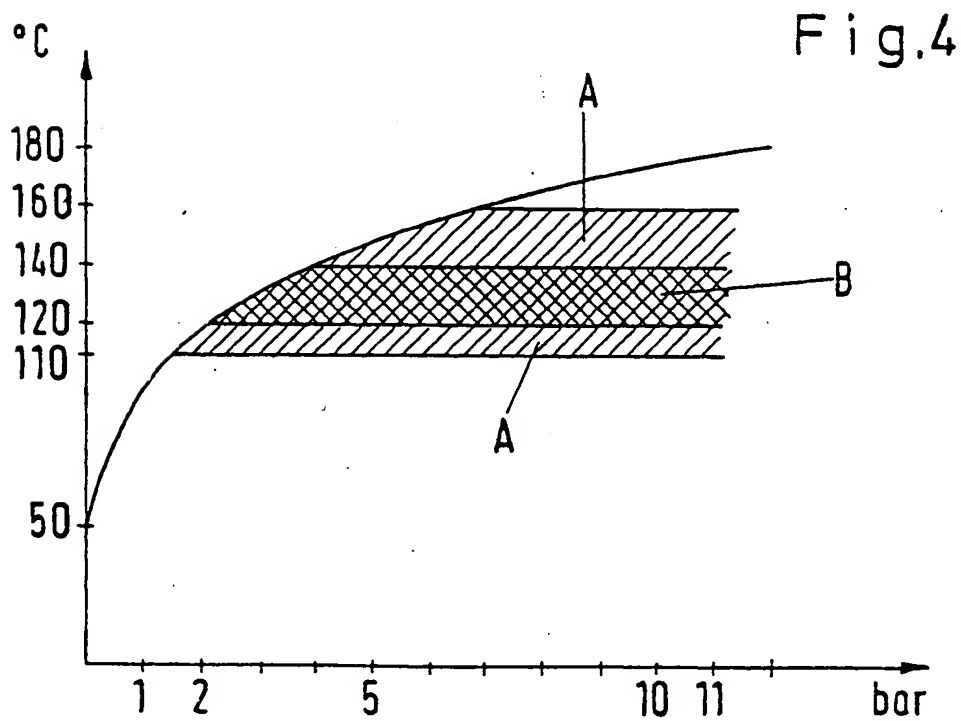
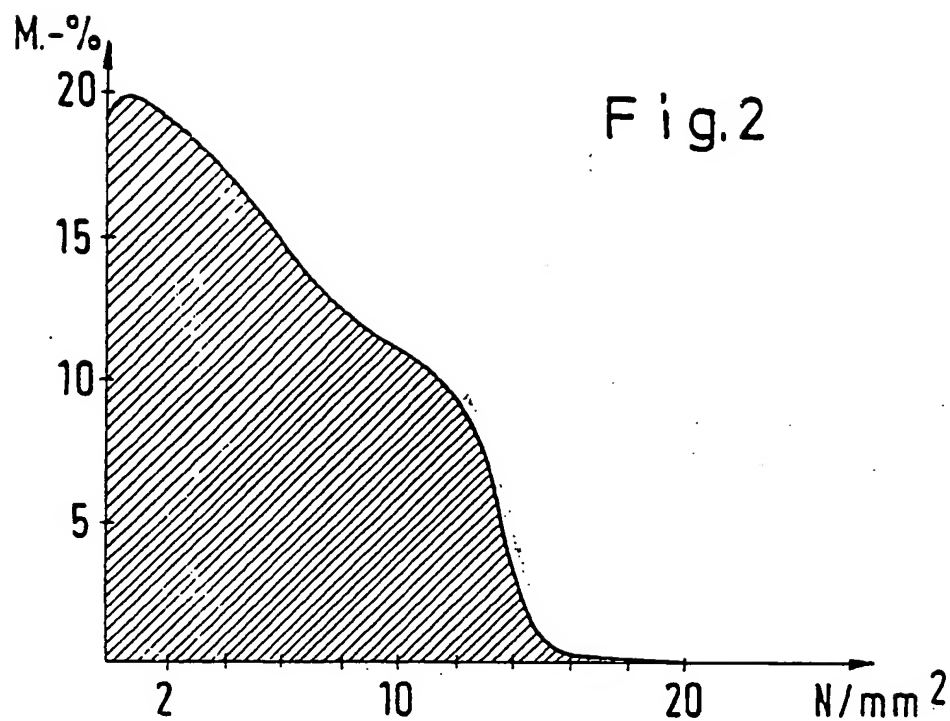
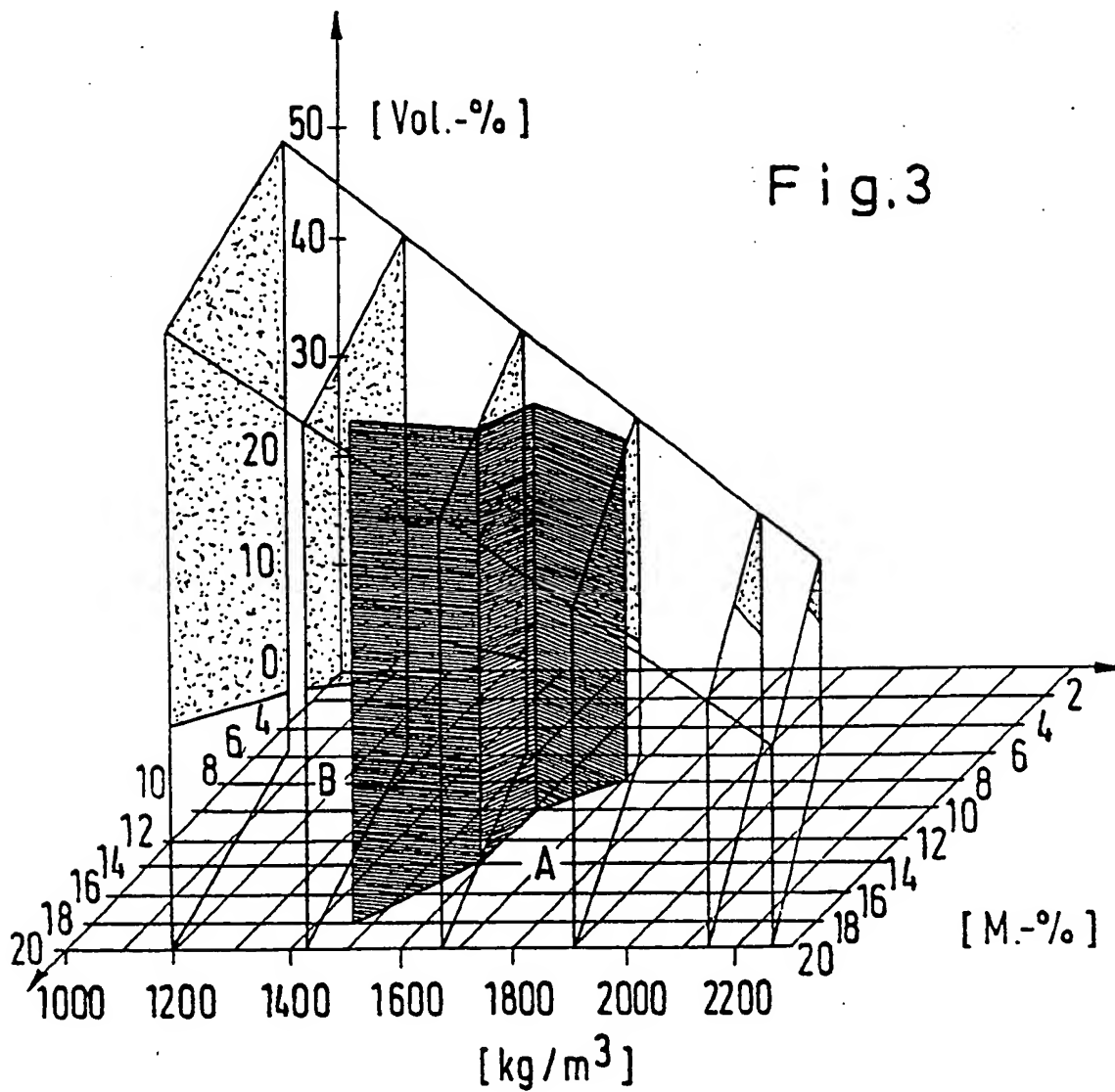


Fig. 1



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Fig.5

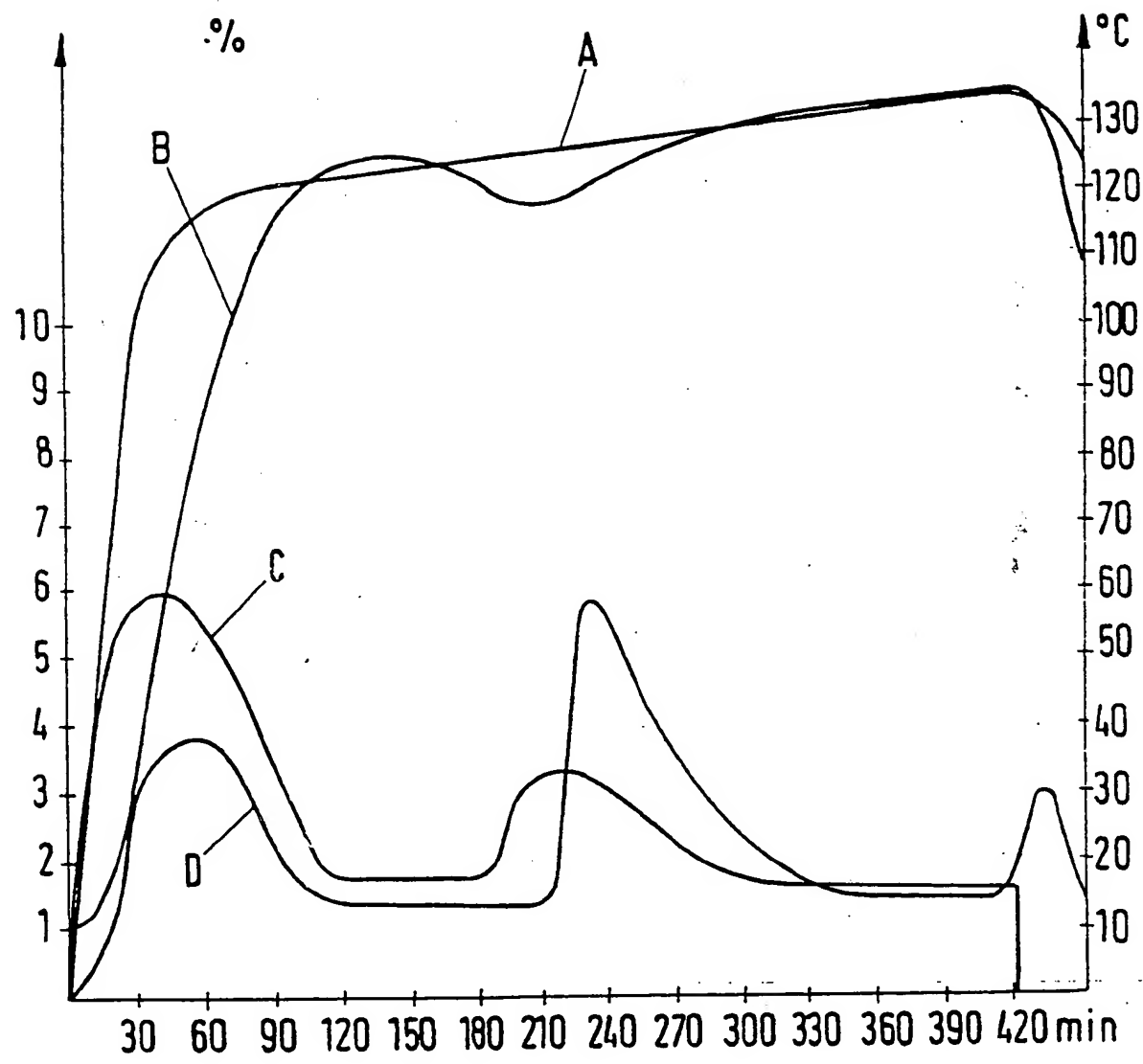
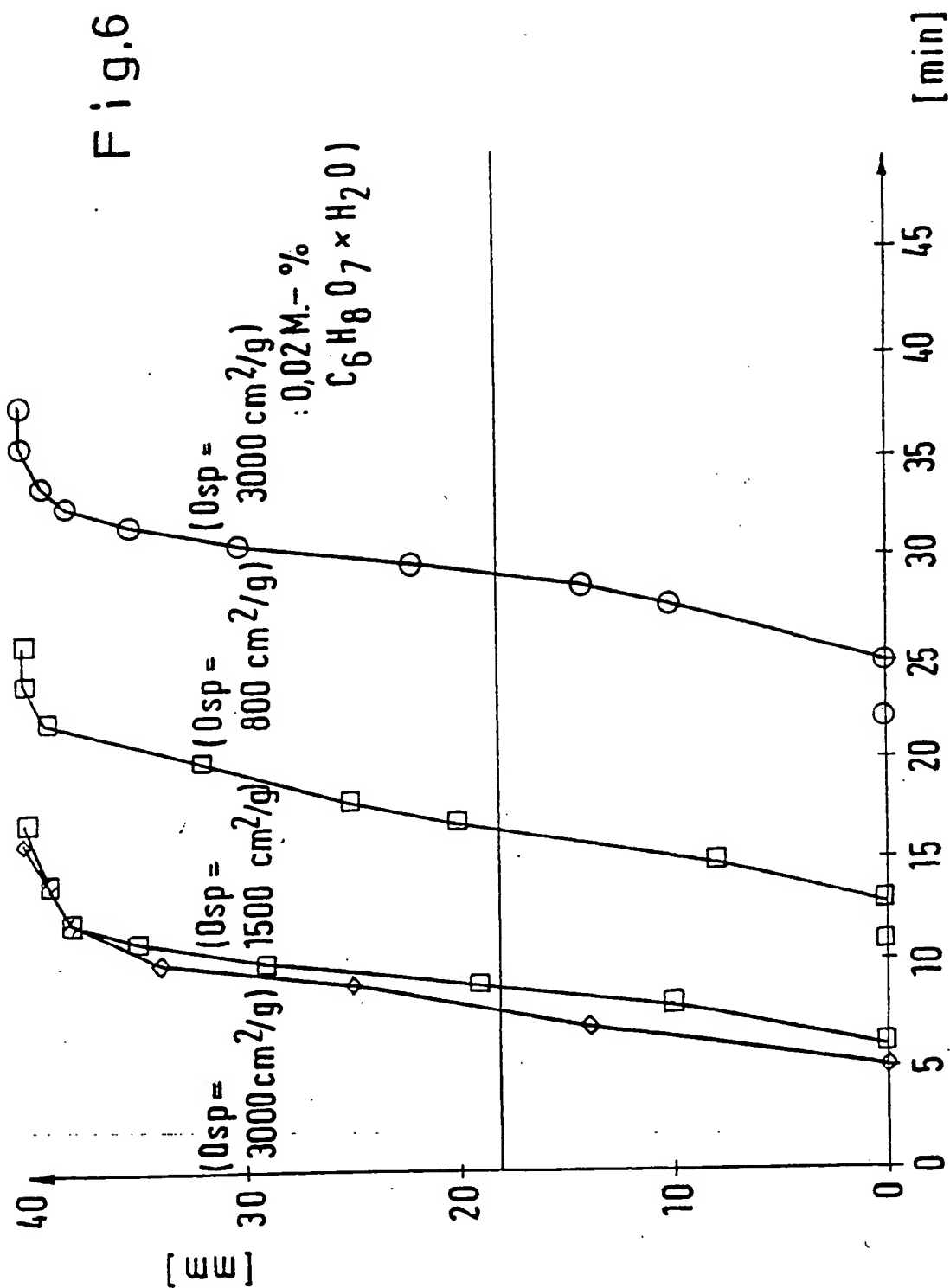
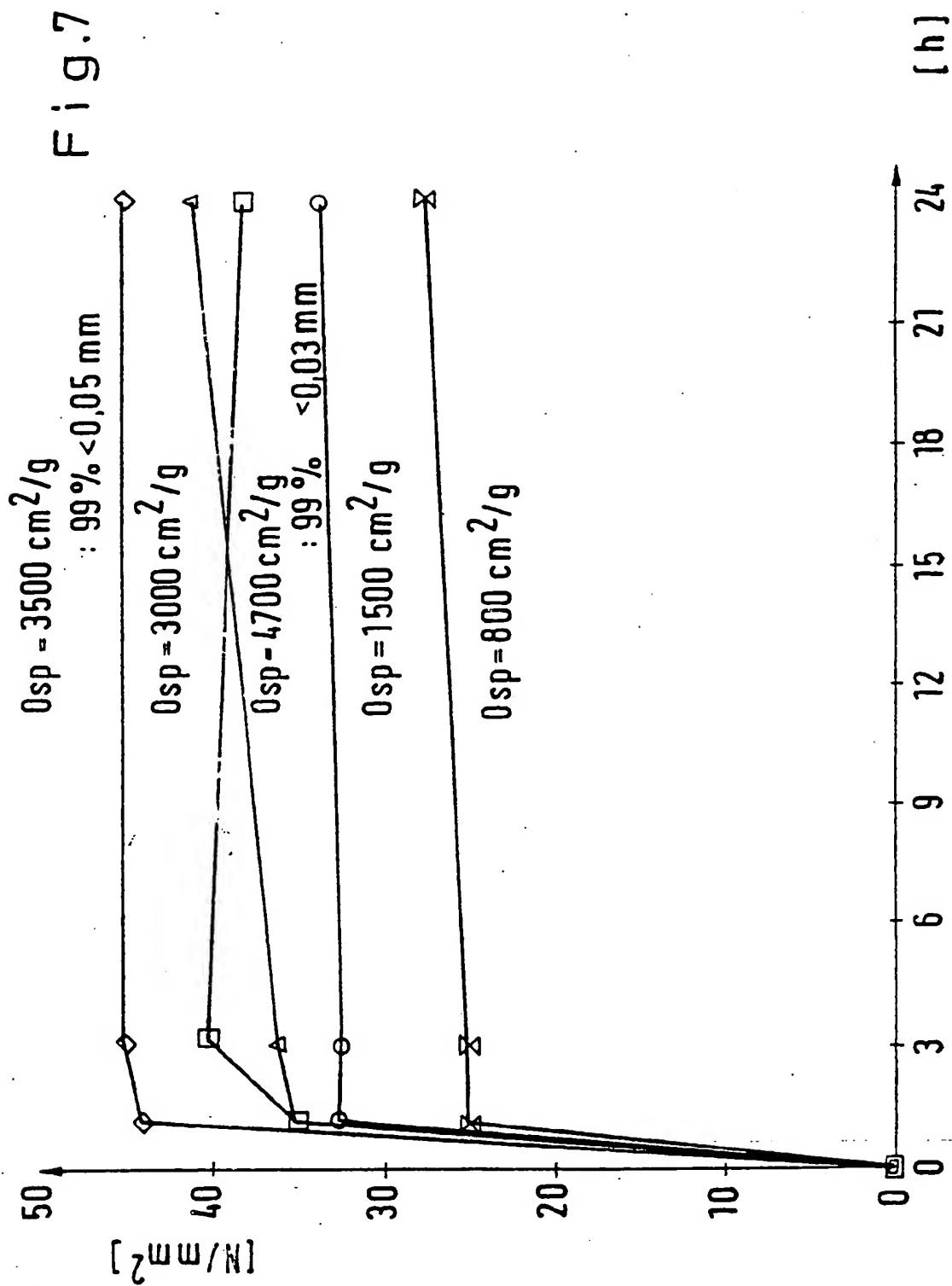


Fig.6





## PROCESS FOR PRODUCTION OF CALCIUM SULPHATE ALPHA-HEMIHYDRATE

This invention relates to a process for the production of calcium sulphate alpha-hemihydrate from finely divided calcium sulphate dihydrate by recrystallising the calcium sulphate dihydrate in the presence of saturated water vapour. The calcium sulphate dihydrate used in the process of the invention can be of any origin. It can be a mineral gypsum or a gypsum produced by synthesis. The resulting calcium sulphate alpha-hemihydrate can be used for a variety of purposes, for example as a building material or a filler.

There are numerous known processes for the conversion of calcium sulphate dihydrate to calcium sulphate alpha-hemihydrate. The invention relates to a certain known process for the production of the alpha-hemihydrate from mineral gypsum (Ullmanns Encyklopadie der technischen Chemie, vol. 12, 1976, p.301,) in which lumps of calcium sulphate dihydrate, or in other words mineral gypsum, are placed in an autoclave and therein converted to lumps of calcium sulphate alpha-hemihydrate in the presence of saturated water vapour at a temperature of 130 to 135 °C, the product being dried at a temperature above the stability limit for calcium sulphate dihydrate and then milled for further use. In more detail, the procedure is as follows: Rock gypsum from a naturally occurring deposit is crushed to a lump size of 150 to 300 mm, and baskets full of lumps are set up in an autoclave. The latter is heated directly or indirectly by steam at 130 to 135°C. [The heating stage is controlled so that, in conformity with the saturated-steam curve, a pressure of 4 to 5 bar is attained after about 4 hours. The autoclave is

then emptied. The product, calcium sulphate alpha-hemihydrate, is transferred in the baskets to an oven, dried under normal pressure at about 105°C and finally milled to a fine powder. The surface layers of the lumps are found to contain distinct crystals of calcium sulphate alpha-hemihydrate, which have grown into more or less acicular forms. The cores of the lumps after the autoclave treatment are found to contain structurally diffuse crystal forms, still accompanied by calcium sulphate dihydrate residues, even after very long treatment periods. Neither the crystal form nor the fine surface structure is controllable under the known processing conditions. The term "crystal form" covers both the size and the facetting of the crystal faces. The term "fine surface structure" covers the topography of the crystal facets. The quality of the calcium sulphate alpha-hemihydrate produced in this way is open to improvement in these respects.

In the case of so-called chemical gypsum, which is produced in finely divided form during the production of phosphoric acid for example (Ullmanns Encyklopadie der technischen Chemie, loc. cit., pp. 303 & 304), the raw chemical gypsum is prepared as a suspension or sludge in water and subjected to a flotation treatment to remove organic impurities. Next, the water-soluble and removable water-insoluble impurities are removed by counterflow washing in a washing tower or hydro-cyclone. The resulting gypsum/water sludge is pumped continuously into an autoclave and converted to calcium sulphate alpha-hemihydrate at a temperature of about 150°C and a corresponding saturated

steam pressure. Additives to control the pH value and vary the crystal form can be dispensed into the autoclave, so that it is possible in theory to produce alpha-hemihydrate gypsum in a variety of grades. The disadvantages of this known process include the costliness of the purification stages and the large volumes of water required for the crystallisation stage, which lead to disposal and drying problems. Moreover, the crystal form of the calcium sulphate alpha-hemihydrate is even more variable and no means are provided for controlling the process in respect of crystal form and fine surface structure. Furthermore, the conversion yield is unsatisfactory. The production of calcium sulphate alpha-hemihydrate having specific properties for specific application, on the other hand, involves the control of crystal forms and fine surface structures within determined and specifiable ranges.

The object of the invention is to provide a process for the production of calcium sulphate alpha-hemihydrate from finely divided calcium sulphate dihydrate, whereby the products consist of calcium sulphate alpha-hemihydrate crystals of substantially completely uniform form, and the processing parameters can be controlled to obtain a range of specific and reproducible properties in respect of crystal form and fine surface structure.

According to the present invention, this object is achieved in a process for the production of calcium sulphate alpha-hemihydrate from finely divided calcium sulphate dihydrate by recrystallising the calcium sulphate dihydrate in the presence of saturated water vapour, in which process

the calcium sulphate dihydrate is prepared in the form of mouldings containing 15 to 60 vols.% of pores and at least 5 vols.% of air in the pores (all percentages relating to the volume of a single moulding), the mouldings are placed in an autoclave, in the presence of a sufficient amount of water in the pores, the crystal growth and crystal form of the calcium sulphate alpha-hemihydrate, which grows in and from an aqueous solution phase, are controlled by maintaining a temperature between 110°C and 180°C and regulating the atmospheric pressure inside the autoclave, and after recrystallisation the mouldings are taken out of the autoclave and used as required.

To make use of the autoclaved mouldings, they are usually dried first, at a temperature above the thermal stability limit for calcium sulphate dihydrate and then prepared for use by milling or sieving for example. They are preferably dried to below 1 wt.% water. The mouldings are prepared in a manner that produces an open capillary pore system.

Within the scope of the invention, various methods can be adopted to ensure that the pores will contain a sufficient amount of water. In this connection, the invention makes use of the fact that mouldings prepared from finely divided calcium sulphate dihydrate and containing the specified volumes of pores have a high capillary water absorption capacity and can therefore absorb water of condensation. Still in this connection, one preferred embodiment of the invention is characterised in that the mouldings are placed in the autoclave at room temperature or slightly higher, so

that water of condensation is deposited on their surfaces from the saturated water vapour and is then drawn into the pores in the mouldings by capillary action. Generally speaking, at least part of the water in the pores consists of water contained in the finely divided calcium sulphate dihydrate from which the mouldings are made, for example as residual moisture. The minimum necessary or optimum amounts of physically bonded water can easily be determined by experiment. It should usually amount to a few wt.% at the start of recrystallisation.

By virtue of operation of the process in accordance with the invention, the mouldings are converted very completely and very uniformly into calcium sulphate alpha-hemihydrate in the form of similarly shaped crystals of controllable form, with no danger of disruption by cracking or loosening. This is surprising, in that the known process initially described for the production of hemihydrate gypsum from mineral gypsum produces structures of diffuse crystal form in the cores of the individual lumps of gypsum rock and the conversion yield is unsatisfactory. The effect obtained by the invention arises from the presence of sufficient water in the pores before the start of recrystallisation, and also the availability in the pores of sufficient space for mass transport into and out of the solution phase.

In connection with the reclamation of gypsum from gas desulphurisation installations for use as a building material, it has already been proposed (DE-PS 35 02 637) to prepare the said gypsum in the form of mouldings, which are then calcined by the action of saturated or superheated

steam, under atmospheric or excess pressure, without using an autoclave. It is not thought necessary in this case to provide controlled conditions for recrystallisation into a specified crystal form. It is beyond the scope of the known process to produce calcium sulphate alpha-hemihydrate of a specified crystal form, or to control the crystal form. The same applies to a similar known process (DE-PS 31 17 662), which takes gypsum from gas desulphurisation installations and produces wall building blocks, usually with additions of sand.

Within the scope of the invention there are various possibilities for the further development and adaptation of detailed aspects of the process. For instance, it is preferred to use mouldings with pore volumes between 20 and 50 %. Outstandingly good results are obtained when the mouldings are formed with a pore volume of 25 to 35 %. One aspect of the invention, which has proved very sound, indicates that the mouldings are preferably prepared in such a manner that at least half the pore volume is occupied by air.

Within the scope of the invention, the mouldings can be prepared by a variety of methods. The method of preparation depends on the physical parameters of the finely divided calcium sulphate dihydrate from which the mouldings are made. If it is completely or substantially dry, a suitable binder can be added to the finely divided calcium sulphate dihydrate. The pore volume can be adjusted or influenced by the addition of a foam, in the manner commonly used in the production of lightweight building materials.

If the original calcium sulphate dihydrate contains sufficient physically bonded water, in the form of residual moisture, or if water is added, the calcium sulphate dihydrate mouldings may be made by pressing, at pressures up to  $14 \text{ N/mm}^2$  in the presence of between 3 and 20 wt.% of water; mouldings which remain intact during autoclave treatment are preferably made at pressures between 1 and 5  $\text{N/mm}^2$ , for example at 2-3  $\text{N/mm}^2$ . The preferred pressure becomes higher as the water content of the calcium sulphate dihydrate is lowered, and vice versa, - and the pore volume factor must not be overlooked. These conditions surprisingly produce mouldings which on the one hand contain the volume of pores specified by the invention, and a corresponding volume of water, and on the other hand will remain intact in the autoclave. If briquettes are used, they can be stacked with open joints in the autoclave, with advantages in respect of the control of recrystallisation.

In the process of the invention, it is often necessary to use growth-regulating additives, in keeping with the nature of the supply of calcium sulphate dihydrate, in common with other known processes for the conversion of calcium sulphate dihydrate to calcium sulphate alpha-hemihydrate. The need arises more particularly when it is required to grow large crystals. The list of suitable additives includes for example such acyclic carboxylic acids as formic, oxalic, malonic, succinic, adipic, fumaric, malic, tartaric, citric, and gluconic, or salts thereof, in the usual amounts. Sulphite lye can also be added. The process of the invention has a surprising capacity for the use as growth-

regulating additives of substances which have never before been used for this purpose. In this connection, the list of preferred growth-regulating additives includes finely milled brown coal and/or peat and/or finely milled wood and/or humic acid and/or timber products producing similar effects on the conversion of calcium sulphate dihydrate. These additives are available in ample amounts and at low prices. The invention is independently significant in relation to these additives. In other words, these additives are suitable for the amelioration of the products of other processes for the conversion of calcium sulphate dihydrate to calcium sulphate alpha-hemihydrate. Finely milled brown coal, peat and/or timber products producing similar effects are preferably milled to a particle size range below 100  $\mu$ m. Milled brown coal for example can be added in amounts between 0.1 and 1.0 wt.%, preferably between 0.5 and 0.7 wt.%. Milled peat can be added in amounts between 0.1 and 1.5 wt.%, preferably between 0.5 and 1 wt.%. Timber products producing similar effects also covers wood flour, to be added in amounts between 0.3 and 2.0 wt.%, preferably between 0.7 and 1.5 wt.%. Humic acid can be added as a timber product in amounts between 0.1 and 1.0 wt.%, preferably between 0.3 and 0.7 wt.%. Sulphite lye is active as a growth-regulating additive in amounts between 0.1 and 3.0 wt.%, preferably between 0.5 and 2 wt.%. One can also use sulphite lye products having similar effects, or secondary products from the processing of natural lignin, in amounts between 0.1 and 1.5 wt.%, preferably between 0.3 and 1.2 wt.%. Finally, the list of possible additives includes lignin sulphonates, used

in amounts between 0.1 and 1.2 wt.%, preferably between 0.3 and 0.8 wt.%. A further growth-regulating feature of the invention consists in that a proportion, for example at least 25 wt.%, of the calcium sulphate dihydrate to be converted consists of gypsum from gas desulphurisation installations in power stations fired on brown coal.

When it is required to grow acicular crystals of calcium sulphate alpha-hemihydrate at high conversion rates, it is recommended that the process be operated mainly at temperatures above 140°C.

Conversely, when it is required to grow squat columnar crystals of calcium sulphate alpha-hemihydrate, the operating temperature can be kept mainly within the range 120°C to 140°C. The adverb "mainly" signifies that the conversion temperature can be outside the specified range for a brief period, particularly during the stage preceding the start of recrystallisation.

If the operating temperature exceeds 140°C to 160 °C, increasing proportions of the product, depending on the temperature attained, will consist of smaller and more slender needles of anhydrous calcium sulphate. At temperatures above 160°C and longer treatment periods, increasing proportions of anhydrous fragments will be produced.

Under all the conditions specified above, and over all the indicated temperature ranges, the crystal form can be further influenced by varying the pressure set up in the autoclave, and when it is required to produce squatter crystals of calcium sulphate alpha-hemihydrate within the

indicated range of crystal forms the autoclave pressure should be increased, for which purpose a gas can be pumped into the autoclave. It is self-evident that under this rule specific rectystallisation effects require constant conversion pressures, though it is still possible to vary the pressure during the conversion process.

Under the rules as specified, the mouldings are prepared so as to resist disintegration during the autoclave treatment. In the majority of cases, no special precautions are required. Nevertheless, it is within the scope of the invention to provide for the addition of a binder to the calcium sulphate dihydrate before preparing the mouldings, should this prove necessary. One suitable binder is calcium sulphate alpha-hemihydrate itself, added in a particularly finely divided form in amounts up to 5 wt.% for example. In order to adjust the pore volume, the calcium sulphate dihydrate can be treated with a suitable foam, in the manner known in the production of lightweight building materials.

Calcium sulphate alpha-hemihydrate prepared in accordance with the invention and in milled and sieved form can be used in various sectors of technology, some specific possible applications being as a binder for rapidly setting constructional materials in underground workings, more particularly in tunnels and galleries, and on rockfaces exposed during underground mining operations, or as a binder for self-levelling flooring cement; as a setting agent in rapid repair mortars for the rapid repair of concrete and asphalt roofs; as a material for the production of fibre-

production of foamed porous gypsum slabs for party walls; for the production of foamed porous lightweight gypsum additives for calcium silicate products; for the production of foamed porous adsorbents for use as oil binders, solvent binders or livestock bedding, or for the production of moulds for ceramic products.

Various aspects of the invention will now be described with reference to the accompanying drawings, in which:

Figure 1 shows schematically an installation for carrying out processes in accordance with the invention, merely by way of non-limiting example;

Figure 2 shows the relationship between the initial water content of the calcium sulphate dihydrate and the pressure required to produce mouldings which can be stored, stacked and autoclaved without disintegrating;

Figure 3 shows the relationship between the total porosity of calcium sulphate dihydrate mouldings and their initial density and water content, subdivided into pores filled with air (dotted areas) and water (clear areas) respectively, together with the limits (cross-hatched) of the ranges within which the mouldings can be autoclaved without cracking;

Figure 4 shows the stability range for alpha-hemihydrate produced in accordance with the invention, as a function of temperature and pressure;

Figure 5 shows the variations in time of various important factors during autoclave treatment;

Figure 6 shows the relationship between the setting of alpha-hemihydrate suspensions and the particle size analysis;

and

Figure 7 shows the influence of particle size on the strengthening of pastes prepared from calcium sulphate alpha-hemihydrate produced in accordance with the invention.

The installation shown in Figure 1 includes a stock silo 1 for calcium sulphate dihydrate supplied in the form of gypsum from gas desulphurisation installations. The calcium sulphate dihydrate in the stock silo 1 is fed by a dispenser 2 into a mixer 3, which is also equipped with a dispenser 4 for any necessary additives, which are stored in a corresponding stock silo 5. The mixer 3 delivers the calcium sulphate dihydrate to a hopper 6, from which it is fed to a moulding press 7. The moulding device 7 can be a press for the compaction of say rectangular mouldings, an extrusion press followed by a cutter to chop the ribbon emerging from the extruder into lengths, or a granulator can be used for example in the production of pellets, or even a diecasing unit with vibratory compaction and chemical binding means.

In the moulding press 7, the calcium sulphate dihydrate is formed into mouldings which can be stored, stacked and autoclaved without disintegration, and which contain 15 to 60 vols.% of pores and at least 5 vols.% of air in the pores, when the raw material is moist and the rest of the pore volume is filled with water. The mouldings, in the form of blocks, briquettes or pellets - in suitable basket in the latter case - are set up by a stacker 8 on pallets, arranging them so as to expose the largest possible area of

batch autoclave 9 and treated at temperatures between 110°C and 180°C, until they are substantially completely converted in the saturated vapour to crystals of calcium sulphate alpha-hemihydrate. Suitable air locks can be provided if required when loading and unloading pallets laden with mouldings into and out of the autoclave 9.

The autoclaved mouldings are then dried in a drying unit 10 to an equilibrium moisture content, for example below 1 wt.%. crushed in a crusher 11 and finally milled to the particle size appropriate to their intended use, in a mill 12. Between leaving the autoclave 9 and entering the silo 13 after leaving the mill 12, the calcium sulphate alpha-hemihydrate is held at above about 45°C. i.e., above the thermal stability limit of calcium sulphate dihydrate, to prevent reversion. Crushing can be carried out in a hammer mill for example. The drying unit 10 can be located beyond the crusher 11, and can be in the form of a fluidised bed drier for example. If required, crushing and drying can be carried out in a single step. The mill 12 can for example be a disintegrator, a ball mill or a peg mill, followed in each case by a screen.

The diagram in Figure 2 shows the permissible range of moulding pressures (cross-hatched) as a function of the moisture content of the calcium sulphate dihydrate, which is indicated on the vertical scale in wt.% water; the pressures are indicated on the horizontal scale in N/mm<sup>2</sup>. Mouldings pressed under these conditions can be stored, stacked and autoclave without cracking. The incoming calcium sulphate dihydrate is preferably moulded at its initial water content,

which usually lies between 5 and 20 wt.%. However, if for any reason it exceeds about 20 wt.% it is possible to include preliminary drying so as to keep within the cross-hatched region in Figure 2. The preferred pressure range is between 0.1 and 14 N/mm<sup>2</sup>, better still between 1 and 5 N/mm<sup>2</sup> and optimally between 2 and 3 N/mm<sup>2</sup>.

If the operating conditions are to the right of the cross-hatched region in Figure 2, mouldings will still be produced, but they will crack during autoclaving and thus disintegrate in the autoclave. Still further to the right in Figure 2, at any higher pressure, the mouldings will adhere to the press tools, and increasing pressures will eventually squeeze the material out of the tools.

A sand-lime brick press adjusted to a suitably low pressure can be used to prepare the pressed mouldings. Depending on its magnitude, the application of pressure may squeeze some water out of the calcium sulphate dihydrate. The pressure must therefore be adjusted so that the parameters remain within the cross-hatched region in Figure 2, with further reference to dewatering. As a basic rule, higher initial water contents increase the risk of cracking during autoclaving, and lower compaction pressures reduce the risk of cracking during autoclaving.

Instead of preliminary drying when the initial water content exceeds 20 wt.% of the calcium sulphate dihydrate, and/or as a means of improving the storage and stacking behaviour of the mouldings, one can add a chemical strengthening agent through the dispenser 4, notably up to 5 wt.% of the calcium sulphate dihydrate already produced

by the same process. Alternatively, one can add calcium sulphate beta-hemihydrate or some other non-alkaline fixing agent. This is particularly appropriate when using dies as the moulding equipment. There are no problems in adding these or other substances yet to be specified, since the raw material has a finely divided consistency.

If moulding processes other than those usually adopted in lime-sand brickmaking are used, the pressure can be replaced as a parameter by the initial density or water content of the mouldings, as indicated by the diagram in Figure 3. Starting from the density of pure gypsum ( $= 2.315 \text{ g/cm}^3$ ), the initial density and water content are determined by the volume of air-filled and possibly water-containing pores in the mouldings. The clear areas in Figure 3 denote the volume of water-filled pores and the dotted areas the volume of air-filled pores. The cross-hatching indicates the boundary between mouldings which can be autoclaved without cracking (boundary B for the lower limit) and those which will crack during autoclaving (boundary A for the upper limit). Generally speaking, the mouldings can be autoclaved without cracking when the volume of air-filled pores exceeds that of water-filled pores. Thus, Figure 3 indicates the total and proportionate pore volumes required for crack-free autoclaving.

Figure 4 is a pressure/temperature diagram showing the relationship between the water vapour pressure and temperature in an autoclave containing saturated water vapour. Moreover, Figure 4 indicates the stability range (A+B) and the preferred operating range (B) for the

production of calcium sulphate alpha-hemihydrate. The product can be made at temperatures between 110°C and 160°C, with brief intervals at up to 180°C, and the operating pressure in the autoclave can be increased to well above the saturation water vapour pressure corresponding to the operating temperature by introducing compressed gases.

For the production of calcium sulphate alpha-hemihydrate with a favourable crystal habit, i.e., in large squat single crystals (primary grains) of mostly columnar form with average grain sizes (column lengths) between 250 and 1000  $\mu\text{m}$ , the preferred operating range is between 120°C and 140°C. Calcium sulphate alpha-hemihydrate produced under these conditions is also superior in quality in that it consists of very large primary grains (column length) with deeply notched crystal facets. These promote high reactivity and correspondingly good processing characteristics: mortars and pastes solidify and develop strength within a short period when they are made from this type of calcium sulphate alpha-hemihydrate.

The production of calcium sulphate alpha-hemihydrate at higher synthesis pressures i.e., to the right of the water vapour pressure curve in Figure 4, leads to the formation of still squatter crystals with a low specific surface area. These grades are advantageously used for the preparation of mortars and pastes in cases which primarily require a low water addition, good workability and high strength.

Processing within range B leads to a very uniform crystal habit, and the crystal facets can be made even smoother and more uniform by increasing the pressure beyond

that saturation water vapour pressure by introducing a gas under a suitably high pressure. At higher temperatures between 140°C and 160°C, the reaction rate is increased, i.e., shorter autoclaving periods can be used, while the crystals of calcium sulphate alpha-hemihydrate adopt an increasingly acicular habit and are accompanied by increasing proportions of smaller and more acicular crystals of anhydrous calcium sulphate.

On operating at temperatures below 120°C and approaching 110°C, the columnarity of the crystals gradually decreases and the crystal habit as such becomes more irregular though still homogenous overall.

Crystallising agents and/or crystal growth inhibitors or corrosion inhibitors, added to the calcium sulphate dihydrate before preparing the mouldings, influence the crystal form and fine surface structure of the resulting calcium sulphate alpha-hemihydrate on the one hand and the technological properties of the end products on the other hand. The latter are also influenced by the milling of the calcium sulphate alpha-hemihydrate, which can be regulated in conformity with the intended product application.

Figure 5 shows the variations in time of the inner autoclave wall temperature (curve A), the temperature inside a moulding measuring 20 x 20 x 9.5 cm (curve B), the percentage water vapour demand (curve C) and the amount of condensate formed in the autoclave condensate traps (curve D). As can be seen from the shapes of curves A and B, the temperature inside the mouldings varies similarly to that at the inner autoclave wall, with only a brief time lag. The

temperature drop inside the mouldings after they have reached a certain autoclaving temperature is brought about by the endothermic conversion reaction, and it is subsequently corrected as more water vapour becomes available. Curve C shows the water vapour demand as a function of time spent in the autoclave. It can be seen that the initial water vapour demand is high, since the autoclave contents must be brought up to the operating temperature. The water vapour demand then falls to a lower level corresponding to the compensation for losses. Next, more water vapour is required to compensate for the endothermic nature of the conversion reaction. Finally the water vapour demand falls back to the loss compensation level. Curve D shows the amounts of condensate formed in and removed from the autoclave as a function of time. The first peak relates to condensate formed on the autoclave walls and other metal components, and the difference between the water vapour demand (curve C) and the condensate yield (curve D) during this period relates to the water absorbed by the mouldings during heating, which they initially retain. The curve then falls to a lower level corresponding as in curve C to loss compensation. As the material is converted to relatively large crystals of calcium sulphate alpha-hemihydrate and the specific surface area of the porous mouldings is reduced, larger volumes of condensate are released (with a time lag relative to the start of the conversion reaction, because among other things the condensate takes some time to reach the condensate traps in the autoclave). The volume of condensate is proportional to the reduction in specific surface area. Large squat

crystals with a low specific surface area yield relatively large amounts of condensate, while smaller or more elongated crystals with a correspondingly larger specific surface area yield correspondingly smaller volumes of condensate. The formation of condensate ceases when the conversion reaction reaches completion. The condensate contains water-soluble salts or suspended matter from the raw material, thereby reducing the residual contents thereof in the end product, and depending on the nature enhancing the quality of the end product. In this connection, it should be pointed out that the condensate consists not only of water contained in the pores of the mouldings as a result of using moist raw materials, and/or condensate from the water vapour absorbed prior to the conversion reaction, but also includes the water of crystallisation lost by the calcium sulphate dihydrate during the conversion reaction. The third peak on curve D reflects the fact that at the end of the autoclave treatment the autoclaved pressure is lowered, with the result that the mouldings remain at a higher pressure because of the air they contain and the reversion of condensate to water vapour in the pores, and at least a proportion of the water still contained in the mouldings is expelled by the pressure gradient from the core to the surfaces of the mouldings. In this connection, the pressure must not be released too rapidly or too far, since this might cause the mouldings to burst open. In this way, a further dewatering is brought about which reduces the subsequent drying costs. Moreover foreign matter still dissolved or in suspension is partially expelled. The resulting alpha-hemihydrate is milled in

conformity with the intended application. The degree of milling influences both the stiffening behaviour and the strengthening of calcium sulphate alpha-hemihydrate mixtures with water.

Figure 6 shows the stiffening behaviour of suspensions of calcium sulphate alpha-hemihydrate as a function of the degree of milling; the vertical scale denotes the needle reading (in mm) on a Vicat tester conforming to DIN 1168, and the horizontal scale denotes the time lapse (in min). It clearly shows that as the specific surface area  $\sigma_{sp}$  is increased the incubation period before stiffening is shortened. Consequently, the addition of an inhibitor to prolong the working period, in the form of citric acid monohydrate for example, is recommended for at least the grades of calcium sulphate alpha-hemihydrate milled to a high specific surface area. Thus for example, the incubation period before stiffening starts, for an alpha-hemihydrate of specific surface area  $3000 \text{ cm}^2/\text{g}$ , is prolonged from about 7 min to about 30 min by the addition of 0.02 wt.% citric acid monohydrate.

As Figure 7 shows, the degree of milling influences the strength. The vertical scale in Figure 7 denotes the compressive strength in  $\text{N/mm}^2$  and the horizontal scale the time lapse in hours, while the various curves relate to alpha-hemihydrate pastes made from alpha-hemihydrates with the quoted specific surface areas, in each case with the addition of 0.02 wt.% citric acid monohydrate. The alpha-hemihydrates with specific surface areas of 3500 and 4700  $\text{cm}^2/\text{g}$  were stored in the water demand in these cases

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expressed as the ratio of water to gypsum (W/G) was 0.28.

# CLAIMS

1. A process for the production of calcium sulphate alpha-hemihydrate from finely divided calcium sulphate dihydrate by recrystallising the calcium sulphate dihydrate in the presence of saturated water vapour, in which process the calcium sulphate dihydrate is prepared in the form of mouldings containing 15 to 60 vols.% of pores and more than 5 vols.% of air in the pores (all percentages relating to the volume of a single moulding), the mouldings are placed in an autoclave, in the presence of a sufficient amount of water in the pores, the crystal growth and crystal form of the calcium sulphate alpha-hemihydrate, which grows in and from an aqueous solution phase, are controlled by maintaining a temperature between 110°C and 180°C and regulating the atmospheric pressure inside the autoclave, and after recrystallisation the mouldings are taken out of the autoclave and used as required.

2. A process as in Claim 1, in which the mouldings are placed in the autoclave at room temperature, so that water of condensation is deposited on their surfaces from the saturated water vapour and is then drawn into the pores in the mouldings by capillary action.

3. A process as in either of Claims 1 and 2, in which at least part of the water in the pores consists of water contained in the finely divided calcium sulphate dihydrate from which the mouldings are made.

4. A process as in any one of Claims 1 to 3, in which the mouldings are made with a pore volume of 25 to

5. A process as in any one of Claims 1 to 4, in which at least half the pore volume is occupied by air.

6. A process as in any one of Claims 1 to 5, in which the calcium sulphate dihydrate mouldings are made by pressing, at pressures up to  $14 \text{ N/mm}^2$  in the presence of between 3 and 20 wt.% of physically bonded water, so that the mouldings will remain intact during autoclaving.

7. A process as in any one of Claims 1 to 6, in which acicular crystals of calcium sulphate alpha-hemihydrate are formed by operating mainly at temperature above  $140^\circ\text{C}$ .

8. A process as in any one of Claims 1 to 6, in which squat columnar crystals of calcium sulphate alpha-hemihydrate are formed by operating mainly at temperatures between  $120^\circ\text{C}$  and  $140^\circ\text{C}$ .

9. A process as in any one of Claims 1 to 8, in which very squat crystals of calcium sulphate alpha-hemihydrate are formed by operating at a pressure higher than the saturated water vapour pressure, for which purposes a gas is pumped into the autoclave.

10. A process as in any one of Claims 1 to 9, in which after recrystallisation at least part of the water contained in the pores in the mouldings is driven out by the controlled release of pressure from the autoclave.

11. A process as in any one of Claims 1 to 10, in which growth-regulating additives are mixed into the calcium sulphate dihydrate before the mouldings are made.

12. A process as in Claim 11, in which the growth-regulated additives mixed into the calcium sulphate dihydrate consist of finely milled brown coal and/or finely milled peat

and/or finely milled wood and/or humic acid and/or timber products producing similar effects.

13. A process as in any one of Claims 1 to 12, in which a proportion of the calcium sulphate dihydrate to be recrystallised consists of gypsum from gas desulphurisation installations in power stations fired on brown coal, as a growth-regulating additive.

14. Calcium sulphate alpha-hemihydrate made by the process as in any one of Claims 1 to 13.

15. Calcium sulphate alpha-hemihydrate as in Claim 14, in milled and sieved form, used as a binder for rapidly setting constructional materials in underground workings or as a binder for self-levelling flooring cement.

16. Calcium sulphate alpha-hemihydrate as in Claim 14, in milled and sieved form used as a setting agent in rapid repair mortars for the rapid repair of concrete and asphalte roofs.

17. Calcium sulphate alpha-hemihydrate as in Claim 14, in milled and sieved form, as a material for the production of fibre- and/or chip-reinforced slab products.

18. Calcium sulphate alpha-hemihydrate as in Claim 14, in milled and sieved form, as a material for the production of foamed porous gypsum slabs for party walls.

19. Calcium sulphate alpha-hemihydrate as in Claim 14, in milled and sieved form, as a material for the production of foamed porous lightweight gypsum additives for calcium silicate products.

20. Calcium sulphate alpha-hemihydrate as in Claim 14, in milled and sieved form, as a material for the

production of foamed porous adsorbents for use as oil binders, solvent binders or livestock bedding.

21. Calcium sulphate alpha-hemihydrate as in Claim 14, in milled and sieved form, as a material for the production of moulds for ceramic products.

22. Processes for the production of calcium sulphate alpha-hemihydrate substantially as hereinbefore described with reference to the accompanying drawings.

23. An installation for carrying out processes in accordance with any of Claims 1 to 13, and 22, substantially as hereinbefore described with reference to Figure 1 of the accompanying drawings as governed by any one or more of Figures 2 to 7.